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## On Fungicidal Activity and Preservative Properties of Organotin Compounds

Koichi NISHIMOTO\* and Goro FUSE\*\*

西本孝一\*, 布施五郎\*\*: 有機錫化合物の殺菌性と防腐性について

Organotin compounds have recently drawn much interest owing to their toxicity and fungicidal activity of wide spectrum. Of possible five kinds of tetravalent tin compounds, those so far known to have fungicidal activity are confined to the types  $R_4Sn$ ,  $R_3SnX$  and  $R_2SnX_2$ . The compounds of these types are also different in fungicidal activity according to their structures, molecular weights, solubilities and so on,  $R_3SnX$  being in general much more active than the other two. Further, the compounds of the type  $R_3SnX$  having different R groups have considerably different fungicidal properties. When R is alkyl, the fungicidal activity of the compounds  $C_2H_5-C_6H_{11}$  is higher, of those having  $C_6H_{13}$  slightly lower, and of those having  $C_8H_{17}$  considerably low. When R is aryl, any compounds having tolyl, benzyl, tri-2-phenyl, naphthyl, pyridinyl or chlorophenyl groups do not show higher fungicidal activity than triphenyltin compounds. However, the effect of altering the kind of X in  $R_3SnX$  on its fungicidal and fungistatic activity has not been investigated.

Wood preservatives are required to be long durable in fungicidal activity. So the question of the stability against sun light (ultraviolet light), namely the change in fungicidal activity after exposure to ultraviolet light, has arisen. For example, organomercury compounds can be used as agricultural chemicals, but their use as wood preservatives is questionable, for they are generally unstable against ultraviolet light.

Their wood preservative properties, however, are not always parallel to these results. Especially, when the weathering treatment are done, different results are sometimes obtained. Therefore, the authors investigated to ascertain the preservative activity of several compounds that seemed effective in the previous work, using soil-block techniques.

In this article are summarized both the results described in "Wood Research" No. 26<sup>1)</sup>, and No. 32<sup>2)</sup> and those reported at the 14th meeting of Japan Wood Research Society.

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## 1. Fungistatic Properties of Organotin Compounds

Of  $R_3SnX$  compounds, especially tributyltin compounds with systematically varied X's were synthesized and the relation between their chemical structures and the activities against wood decaying fungi was investigated. The variation of fungicidal property of several compounds on several fungi was also investigated.

Every method so far proposed for testing fungicidal activity has merits and demerits. The agar dilution method was employed in our experiments, for according to this method the results of relatively small error can be obtained rapidly by simple procedures.

Agar culture medium was prepared from 150 grams of glucose, 15 grams of

Table 1. The toxic limit of each compound against *Corirolellus palustris*.

Compound	Toxic limits (%)	Compound	Toxic limits (%)
Tributyltin chloride .....	0.001 —0.002	Tributyltin hydroxide .....	0.001 —0.002
Tributyltin oxide .....	0.001 —0.002	Tributyltin acetate .....	0.0005—0.001
Tributyltin caprylate.....	0.001 —0.002	Tributyltin laurate .....	0.001 —0.002
Tributyltin palmitate.....	0.002 —0.004	Tributyltin stearate .....	0.002 —0.004
Tributyltin fumarate .....	0.001 —0.002	Tributyltin tartarate .....	0.001 —0.002
Tributyltin citrate .....	0.001 —0.002	Tributyltin ethoxyethyl ether.....	0.001 —0.002
Tributyltin butoxyethyl ether.....	0.002 —0.004	Tributyltin diethylaminoethyl ether.....	0.002—0.004
Tributyltin dicyclohexylaminoethyl ether .....	0.002 —0.004	Tributyltin diethylaminopropyl ether.....	0.002 —0.004
Tributyltin toluate .....	0.002 —0.004	Tributyltin p-hydroxybenzoate ...	0.002 —0.004
Tributyltin salicylate .....	>0.004	Pentaoxyethylene tributyltin salicylate .....	>0.004
Eicosaoxyethylene tributyltin salicylate ether.....	>0.004	Tributyltin terephthalate .....	0.001 —0.002
Tributyltin phthalate .....	0.001 —0.002	Tributyltin isophthalate .....	0.001 —0.002
Tributyltin abietate .....	>0.004	Tributyltin p-nitrophenyl ether...	0.0005—0.001
Tributyltin sulfamate .....	0.001 —0.002	Tributyltin p-toluene sulfonamido .....	0.001 —0.002
Tributyltin p-toluenesulfonate ...	0.001 —0.002	Tributyltin 10-camphor sulfonate	0.001 —0.002
Bis (tributyltin) sulfide .....	0.0005—0.001	Tributyltin $\beta$ -hydroxyethyl mercaptide .....	0.0005—0.001
Tributyltin o, o-dimethyl diphosphoryl acetate .....	0.0005—0.001	S-tributyl stannyl-o, s ethylene trithio phosphate.....	0.0005—0.001
Bis (tributyl stannyl) didodecyl heptathiopyrophosphate .....	0.002 —0.004	Tributyl stannyl didodecyl tetrathio phosphate.....	0.001 —0.002
S-tributyl stannyl o, o-bis (2-ethylhexyl) phosphorodithioate ...	0.001 —0.002	S-tributyl stannyl o, o-bis (polyoxyethylene) phosphorodithioate .....	0.004
Polyethylene glycol tributyltin ether.....	0.004	Tributyltin furoate.....	0.001 —0.002
Tributyltin 5-bromofuroate.....	0.001 —0.002	Tributyltin benzo-thiazolylmercaptide .....	0.001 —0.002

pepton, 112.5 grams of malt extract (Difco) and 3 liters of distilled water. The medium was liquid at 45~50°C. The active ingredient was added to the medium to a given concentration, the mixture was solidified on Petri plates (about 9 cm. in diameter). It had been preliminarily ascertained that the compounds did not decompose, evaporate, or react with the medium compounds during the above procedure. Xylene was employed as the solvent for water insoluble compounds. The solution was emulsified by nonionic surfactants. The agar culture medium containing the active ingredient at a low concentration was let to stand loosely closed in the sterilized room for 24 hours. Then fungus was inoculated and incubated at an appropriate temperature for 7 days, during which the growth of the mycelia was observed. Table 1 shows the toxic limit of each compound against *Corirolellus palustris*.

The change of the residue X in organotin compounds of the type  $R_3SnX$  exercises little influence on their fungicidal properties. It follows that the

Table 2. Toxic limits of some tributyltin compounds for wood-destroying fungi as determined by the agar test.

Fungi	Toxic limits (%)		
	<i>Corirolellus palustris</i>	<i>Merulius lacrymans</i>	<i>Coniophora cerebella</i>
Triethyltin chloride .....	0.003—0.005	0.002—0.003	0.002—0.003
Tributhyltin chloride .....	0.003—0.005	0.002—0.003	0.002—0.003
Tributhyltin oxide .....	>0.005	0.002—0.003	0.003—0.005
Tributhyltin hydroxide .....	>0.005	0.002—0.003	0.002—0.003
Tributhyltin acetate .....	0.005—0.008	>0.005	0.003—0.005
Triphenyltin acetate .....	0.02—0.05	0.01—0.02	0.02—0.03
Dibuthyltin chloride .....	0.02—0.05	0.02—0.03	0.02—0.03
Dibuthyltin oxide .....	>0.05	0.02—0.03	>0.03
Dibuthyltin (dodecathio) tin .....	0.05—0.08	—	—
Dibuthyltin caprylate .....	0.08—0.1	—	—
Dibuthyltin caprate .....	0.005—0.008	0.002—0.003	0.003—0.005
Fungi	<i>Polystictus versicolor</i>	<i>Irpex consors</i>	<i>Polystictus sanguineus</i>
Triethyltin chloride .....	0.002—0.003	0.002—0.003	0.002—0.003
Tributhyltin chloride .....	0.003—0.005	0.003—0.005	0.002—0.003
Tributhyltin oxide .....	0.003—0.005	0.003—0.005	0.002—0.003
Tributhyltin hydroxide .....	0.003—0.005	0.003—0.005	0.002—0.003
Tributhyltin acetate .....	0.003—0.005	0.005—0.008	0.003—0.005
Triphenyltin acetate .....	0.02—0.03	>0.03	0.01—0.02
Dibuthyltin chloride .....	0.02—0.03	0.02—0.05	0.02—0.03
Dibuthyltin oxide .....	0.02—0.05	>0.05	0.02—0.03
Dibuthyltin (dodecathio) tin .....	>0.05	>0.05	0.03—0.05
Dibuthyltin caprylate .....	0.05—0.08	>0.08	0.05—0.08
Dibuthyltin caprate .....	0.002—0.003	0.005—0.008	0.003—0.005

fungicidal property of a organotin compound lies mainly in  $R_3Sn$  moiety. However, it seems that the property is affected more or less by the molecular weight of X or the tin content, the fungicidal property of X itself and so on, a certain degree of difference in fungicidal property of  $R_3SnX$  arising.

The fungicidal activities of several compounds of different types were measured against three fungi causing brown rot and three fungi causing white rot by the agar dilution method as above. The results are shown in Table 2. It was found in this experiment that the organotin compounds in low concentrations still show considerably greater fungistatic toxicity than P.C.P.-Na. The antifungal activity of a wood preservative should not be evaluated by the killing point or total inhibition point only, but it should be estimated by the analysis of spore killing activity, fungistatic toxicity and so on.

The degree of inhibition ( $H$ ) of a compound at a concentration is calculated by the following expression :

$$H = 1 - c_g/c$$

where  $c$  : the growth length of the mycelium on the active ingredient added medium after a given period of incubation (in mm.).

$c_g$  : the growth length of the mycelium on the control medium after the same period of incubation as above (in mm.).

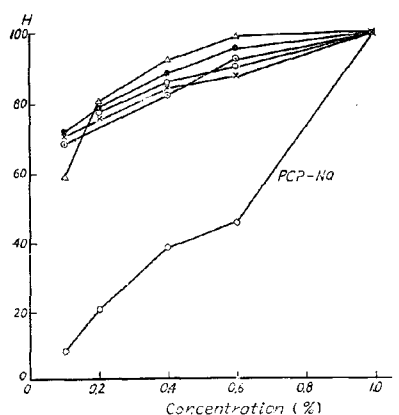


Fig. 1. The relation between the concentration and the degree of inhibition.

- △— p-tolylmercuric p-toluensulfon anilide
- tributyltin chloride
- tributyltin oxide
- ×— tributyltin hydroxide
- ⊙— tributyltin acetate

same tendency as the effect on the fungicidal activity.

## 2. Light Stability of Organotin Compounds

A substance absorbs light at a wave length range characteristic to its molecular structure, and induces a photochemical reaction by the absorbed energy.

A photochemical process comprises two processes: primary process of absorption of light by molecules or atoms, and secondary process of succeeding various transitions of the products formed directly by light absorption. In the primary process a molecule absorbs light and dissociates according to the wave length of the light absorbed to form atoms or free radicals. In the secondary process the atoms or radicals react. Thus molecules of a substance suffer various changes as dissociation, polymerisation etc. by the irradiation of light. Molecules having the absorption band at a short wave length region and involving weak bondages are especially unstable to light and suffer various changes.

The stability against light is thought to be one of the important questions, when an organotin compound is to be used as a wood preservative. In this case, the fungicidal and fungistatic toxicities of the products after the light exposure are rather more important than the photochemical processes involved. Therefore, the authors conducted the following experiments on the change in fungistatic toxicity of organotin compounds by light irradiation with a universal weather meter.

When a compound was water soluble, a 0.1% aqueous solution was prepared, and when water insoluble, it was dissolved in a small amount of xylene and emulsified with an emulsifier into a stable 0.1% emulsion. 10 ml. of the solution or emulsion was put into a special glass tube (1 cm. in inner diameter, 15 cm. long, 1.5 mm. thick, optical pyrex grade), and irradiated with ultraviolet light in the universal weather meter WE-2 (Toyo Rika Kogyo Co.) for 156 hours (equivalent to 9 months natural outdoor exposure), 104 hours (6 months), 52 hours (3 months), and  $17\frac{1}{3}$  hours (1 month).

After the irradiation the concentration of the sample was adjusted precisely to 0.1%, and the growth of the mycelia was observed by the above-mentioned agar dilution method. The fungistatic concentration and the degree of inhibition were determined. The change in the inhibition curves before and after the ultraviolet irradiation was studied.

The results are shown in Figs. 2~10. It will be understood that the light stability of organotin compounds are pretty high, and that tributyltin-terephthalate, toluate, p-toluenesulphonate and furoate which are of the aromatic series, fumarate, and ,o o-dimethyl diphosphorylacetate are show very little change in fungistatic property after the light exposure, the fungistatic toxicity after exposure being much higher than that of chloride, acetate or oxide. Tributyltin hydroxide and sulphamate are slightly lower in light stability than chloride, oxide and so on. After 6 and 9 months exposure, fungistatic activities of the former two are both slightly lower than those of the latter. Water soluble tributyltin sulphamate is supposed to have been affected more by light due to the fact that it was

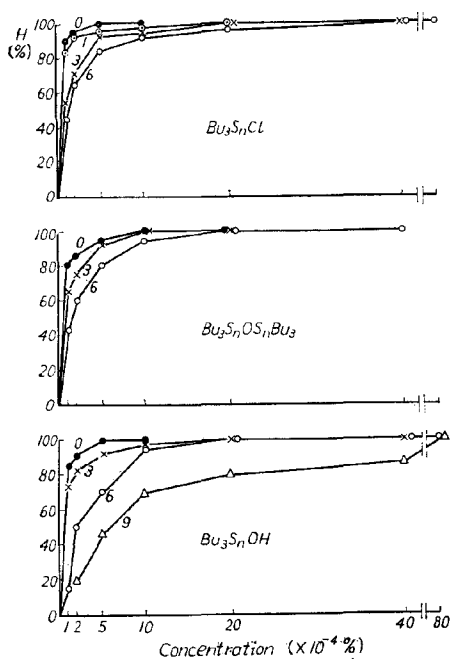


Fig. 2.

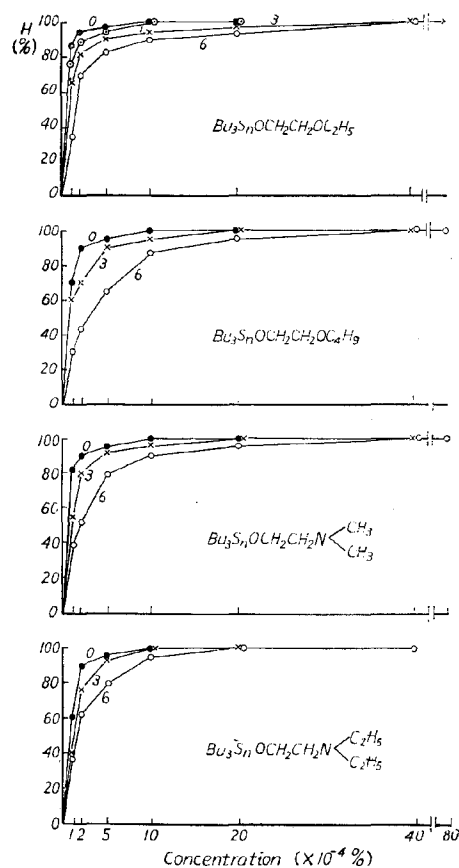


Fig. 3.

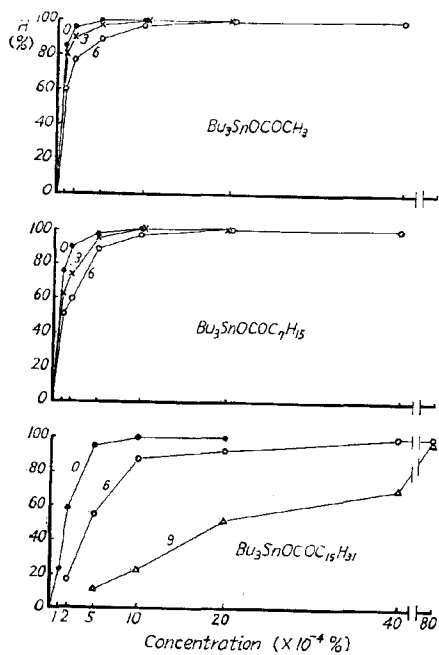


Fig. 4.

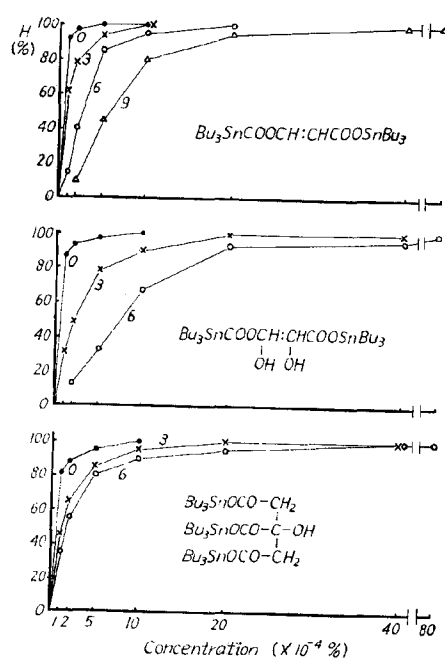


Fig. 5.

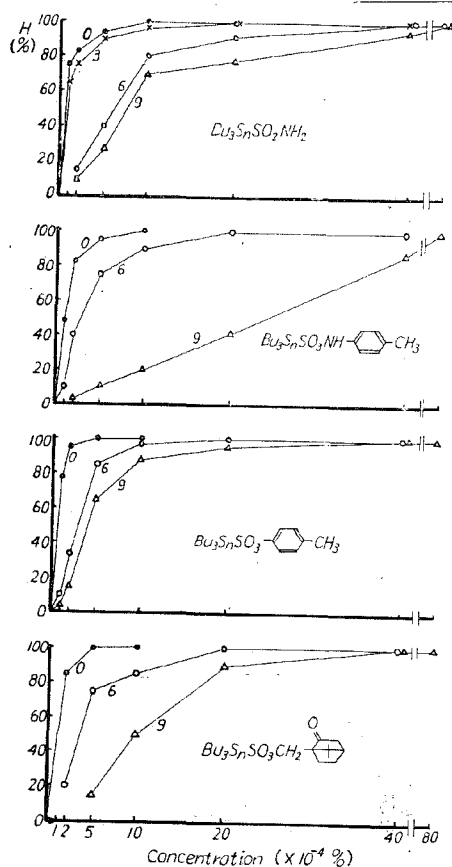


Fig. 6.

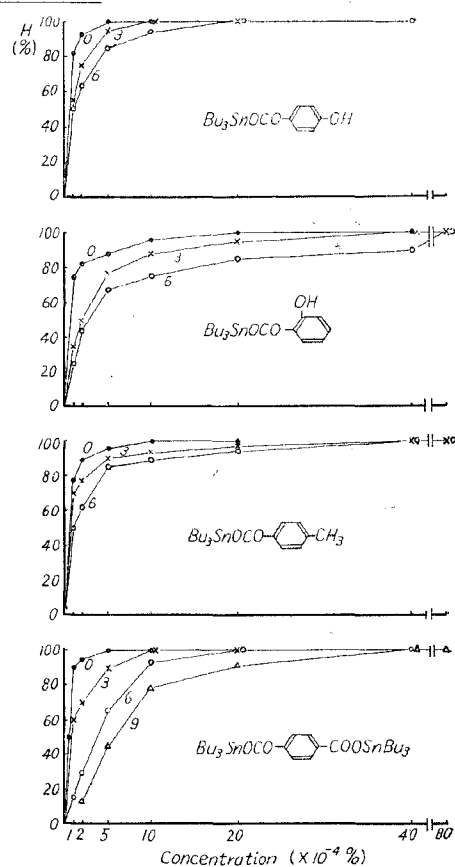


Fig. 7.

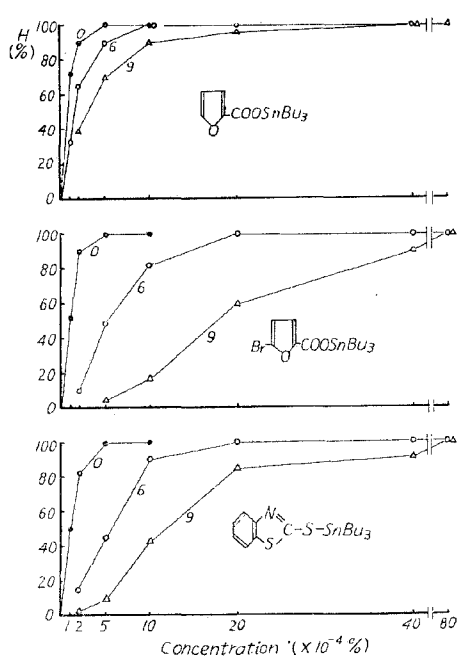


Fig. 8.

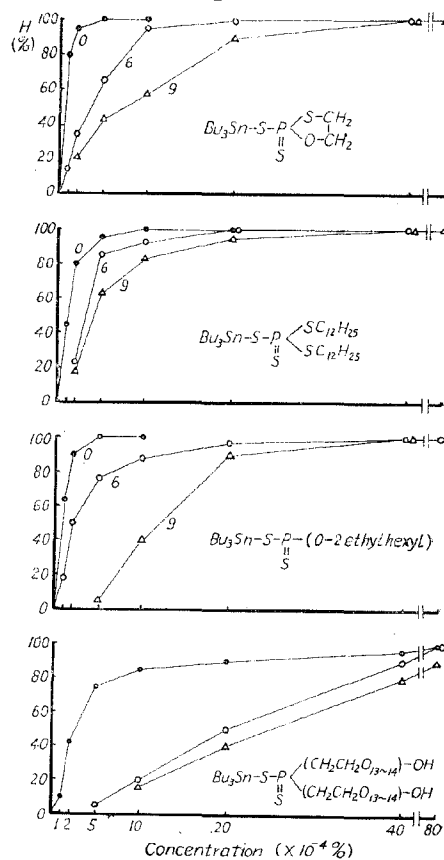


Fig. 9.



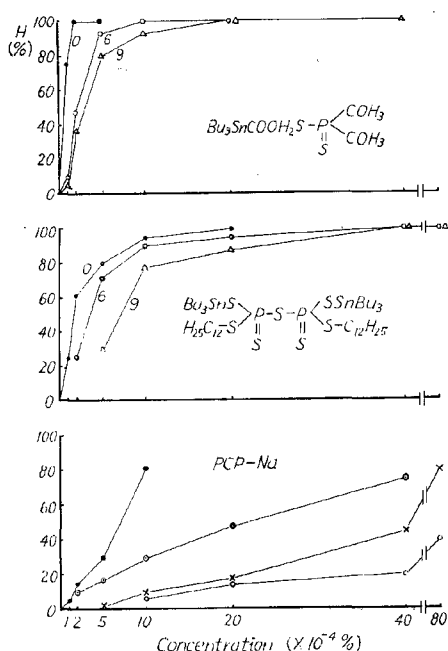


Fig. 10.

pounds, lose little of their toxicity after the irradiation equivalent to 3 months exposure, and decrease slightly in toxicity after 6 or 9 months exposure. This fact indicates that organotin compounds with high light stability are very appropriate to their use as preservatives for green logs or lumbers, and can also be used as preservatives for timbers or boards.

In the figure, the concentration corresponding to 100% inhibition is named the total inhibition point (T.I.P.) of the chemical and the degree of shifting of this point to the right is the question. For example, the T.I.P. of tributyltin furoate lay at 0.0005% before the irradiation but it shifted to 0.001% and 0.004% after 6 and 9 months exposures respectively. The T.I.P. of tributyltin *o*, *o*-dimethyl diphosphorylacetate was originally 0.0002%, after 6 months exposure 0.001% and after 9 months exposure 0.004%. Those of tributyltin fumarate and terephthalate were both the T.I.P. of tributyltin sulphamate and hydroxide shifted from original 0.0005% to 0.002~0.004% after 6 months exposure and to 0.008% after 9 months exposure, the toxicity considerably decreasing. Thus the shift of the T.I.P. is thought to be one of the important measures which give information upon the light stability. The concentrations beyond the 100% inhibition point are the killing points of the chemical.

### 3. Comparison of Effectiveness between Dibutyltin and Tributyltin Compounds

As demonstrated in the previous work dibutyltin compounds (abbreviated to

irradiated in the form of an aqueous solution where the organotin molecule is exposed to greater light energy per molecule than in an emulsion. Fungistatic toxicity of tributyltin polyethylene glycol ether, *o*, *o*-bis (polyoxyethylene) phosphorodithioate, tartarate, *p*-nitrophenyl ether and 5-chlorosalicylate was considerably lowered after the irradiation. The compound having solubilizing long chains was stable to light and the aromatic compound having bromo, chloro, hydroxyl or nitro groups also decreased in fungistatic toxicity. However, even these compounds had pretty higher toxicity than P.C.P.-Na or organomercury compounds. Organotin compounds with high light stability are superior in light stability to organomercury com-

Table 3. Average weight loss and compressive strength loss due to decay in blocks impregnated various compounds.

Concentration (%)	0.5	0.1	0.05	0.5	0.1	0.05
Unweathered blocks						
	Weight loss (%)			Strength loss (%)		
Tributyltin chloride .....	2	2	2	0	7	11
Tributyltin oxide .....	0	2	5	0	1	10
Tributyltin hydroxide .....	1	2	2	0	1	18
Tributyltin acetate .....	2	2	8	1	10	20
Triphenyltin acetate .....	2	14	27	1	38	71
Dibutyltin chloride .....	1	25	23	8	53	54
Dibutyltin dodecathio .....	1	8	15	30	26	37
Dibutyltin caprylate .....	2	18	32	6	44	67
P.C.P.-Na <sup>1)</sup> .....	0	0	2	4	0	9
Creosote <sup>2)</sup> .....	0	2	3	10	2	13
Leached and dried blocks						
	Weight loss (%)			Strength loss (%)		
Tributyltin chloride .....	2	2	5	0	3	19
Tributyltin oxide .....	2	2	6	0	7	20
Tributyltin hydroxide .....	2	2	5	1	3	20
Tributyltin acetate .....	2	5	10	7	6	21
Triphenyltin acetate .....	19	22	20	54	44	57
Dibutyltin chloride .....	29	34	37	58	63	61
Dibutyltin dodecathio .....	2	7	15	11	18	38
Dibutyltin caprylate .....	27	44	38	67	80	80
P.C.P.-Na <sup>1)</sup> .....	3	7	14	10	18	24
Creosote <sup>2)</sup> .....	0	2	4	0	2	14
Weathered blocks						
	Weight loss (%)			Strength loss (%)		
Tributyltin chloride .....	2	2	4	0	8	12
Tributyltin oxide .....	0	2	7	0	3	30
Tributyltin hydroxide .....	1	2	6	0	6	22
Tributyltin acetate .....	1	5	14	5	17	40
Triphenyltin acetate .....	7	20	21	21	47	53
Dibutyltin chloride .....	22	29	39	36	70	87
Dibutyltin dodecathio .....	4	21	36	11	52	63
Dibutyltin caprylate .....	7	25	32	20	63	66
P.C.P.-Na <sup>1)</sup> .....	4	11	12	17	38	42
Creosote <sup>2)</sup> .....	1	3	8	0	7	27

Note. 1) Its concentration : 1. 0.5, 0.1%

2) Its concentration : 100, 20, 10%

DBT) are pretty lower in fungicidal activity than tributyltin compounds (abbreviated to TBT). It is, however, still necessary to clarify the difference in the wood preservative activity against *Corirolellus palustris*. Xylene solution of each compound of a given concentration was injected into a beech block (10×10×20 mm) by the reduced-pressure process until the injected amount reached 200±10 weight %, then the specimen was dried at room temperature for about 4 weeks and weathered. As the weathering methods were employed one according to JIS Standard A-9302 (but 20 repetitions) and one using a universal weather meter<sup>3)</sup>. The weathered and the unweathered test pieces were subjected to the forced decaying for 90 days according to JIS Standard A-9302, and the weight loss and the compression strength decrease were measured.

The results are shown in Table 3. Apparently DBTs is much lower in preservative activity than TBTs. Only DBT dodecathio is comparable to TBTs when the weight losses are compared, yet is somewhat inferior when the strength decreases are compared. Generally when wood decays, carbohydrates such as cellulose and hemicellulose, and lignin also decompose, the wood constituents undergo various changes, and the strength of wood is influenced. The weight of wood may be thought to decrease more as decaying goes on. Therefore, in effectiveness, DBT dodecathio is estimated to take the place between TBTs and other DBTs.

#### 4. Preservative Activities of TBTs (I)

As TBTs were ascertained to be much more effective than DBTs, the preservative activities of TBT oxide, TBT chloride and other 9 compounds shown in Table 4 against *Polystictus sanguineus* were evaluated.

An emulsion of each compound of 0.05, 0.1 or 0.5% concentration was injected by the reduced pressure process into a cedar block (10×10×20 mm) until the injected amount reached 150±10 weight %. The emulsion was prepared by dissolving a compound in xylene and diluting the xylene solution with water by the aid of an appropriate surfactant. After the injection the specimen was dried at room temperature for about 1 month and subjected to the weathering and the toxicity test. The weathering procedure was the same as described above and the toxicity test was done according to JIS A-9302.

The results are shown in Table 4. The retention of each compound was calculated on the assumption that the emulsion was absorbed by wood without any concentration variation. When the retention was 2.8~3.1 kg/m<sup>3</sup>, all the compounds except polyethyleneglycol tributyltin ether showed almost perfect preservation regardless of the weathering. At the retention of 0.57~0.62 kg/m<sup>3</sup>, no

Table 4. Average weight loss (percent) due to decay in blocks at various retentions.

Retention (kg./cu.m. $\times 10^{-2}$ )	28—31	57—62	280—310
Unweathered blocks			
Tributyltin oxide .....	7.2	2.6	2.3
Tributyltin chloride .....	6.3	3.9	0.9
Tributyltin caprylate .....	16.1	6.7	5.8
Tributyltin fumarate .....	3.7	2.8	0.2
Tributyltin citrate .....	8.8	6.6	3.1
Tributyltin ethoxy ethyl ether .....	9.7	5.3	3.7
Tributyltin dimethyl aminopropyl ether ..	7.9	5.7	1.6
Tributyltin toluate .....	6.7	6.9	2.2
Tributyltin parahydroxy benzoate .....	8.3	2.8	1.3
Tributyltin terephthalate .....	7.6	4.9	+1.6
Polyethyleneglycol tributyltin ether .....	26.5	22.3	1.8
Weathered blocks			
Tributyltin oxide .....	15.1	12.7	5.1
Tributyltin chloride .....	13.1	10.5	3.4
Tributyltin caprylate .....	16.3	11.4	5.4
Tributyltin fumarate .....	11.0	5.4	3.0
Tributyltin citrate .....	11.9	6.8	6.4
Tributyltin ethoxy ethyl ether .....	25.8	9.5	4.6
Tributyltin dimethyl aminopropyl ether ..	15.0	7.7	4.0
Tributyltin toluate .....	11.1	11.4	2.9
Tributyltin parahydroxy benzoate .....	13.4	8.8	2.8
Tributyltin terephthalate .....	8.1	6.9	3.0
Polyethyleneglycol tributyltin ether .....	30.6	30.1	21.0
Leached and dried blocks			
Tributyltin oxide .....	7.2	4.3	3.8
Tributyltin chloride .....	12.5	6.3	2.0
Tributyltin caprylate .....	12.2	11.7	3.5
Tributyltin fumarate .....	6.9	4.5	2.5
Tributyltin citrate .....	11.0	6.9	2.4
Tributyltin ethoxy ethyl ether .....	13.3	7.6	1.3
Tributyltin dimethyl aminopropyl ether ..	22.0	13.2	4.9
Tributyltin toluate .....	7.3	6.8	3.9
Tributyltin parahydroxy benzoate .....	6.8	4.5	1.2
Tributyltin teraphthalate .....	7.1	8.1	1.2
Polyethyleneglycol tributyltin ether .....	25.6	23.2	22.6
Control			
	Unweathered	Weathered	Leached
Control .....	29.4	34.0	25.8

significant difference was found with all the compounds when the weathered blocks, TBT fumarate, TBT citrate and TBT terephthalate were superior. At the retention of 0.28~0.31 kg/m<sup>3</sup>, the superiority of TBT fumarate and TBT

terephthalate was more significant and they were only effective. This tendency is parallel to that of the light stability previously reported<sup>2)</sup>.

### 5. Preservative Activity of TBTs (II)

The superior preservative activity of TBT fumarate and TBT terephthalate among various TBTs is evident from the above-mentioned results. In the above-mentioned experiment, however, the emulsion was employed, and therefore, whether the emulsion penetrated into wood as it was, namely retaining the original concentration, is still a question. To avoid this problem and also to ascertain the activity against other fungi, this experiment was conducted. Some interesting phosphor-containing compounds were inclusively tested. Each TBT was dissolved in Swasol (Maruzen Oil Co.), a commercial hydrocarbon mixture solvent (boiling range 104~114°C., aromatic content 76 v/v %), at a concentration

Table 5. Average weight loss (percent) due to decay in blocks.

Fungi Retention (Kg/cu.m. $\times 10^{-2}$ )	<i>Corirolellus palustris</i>			<i>Coriolus versicolor</i>		
	20—25	45—50	240—250	20—25	45—50	240—250
Weathered blocks						
Tributyltin sulfamate*	8.2	1.5	1.6	19.7	5.5	3.4
Tributyltin terephthalate	11.6	1.7	—	—	3.6	—
Tributyltin fumarate	5.6	2.3	0.9	7.3	4.6	2.9
Tributyltin oxide	16.5	0.5	—	10.6	3.8	—
Tributyltin $\beta$ -hydroxy ethylmercaptide	27.6	2.4	0.4	13.8	4.4	2.7
Tributyltin furoate	20.1	4.6	1.2	10.3	5.9	2.6
S-tributyl stannyl-o, s-ethylene trithiophosphate	18.8	3.6	—	7.8	5.8	—
Tributyltin-o, s-dimethyl diphosphoryl acetate	16.8	0.7	0.3	20.0	9.7	2.7
Leached and dried blocks						
Tributyltin sulfamate*	9.4	2.3	3.5	7.9	3.0	3.5
Tributyltin terephthalate	8.1	2.3	—	4.4	3.4	—
Tributyltin fumarate	7.8	2.5	5.3	5.0	5.0	2.7
Tributyltin oxide	15.9	1.6	—	10.2	3.1	—
Tributyltin $\beta$ -hydroxy ethylmercaptide	38.3	2.7	2.8	8.0	5.1	2.6
Tributyltin furoate	35.9	7.8	4.1	10.5	5.1	3.4
S-tributyl stannyl-o, s-ethylene trirhiophosphate	11.6	2.9	—	11.9	8.2	—
Tributyltin-o, o-dimethyl diphosphoryl acetate	20.4	1.8	2.3	9.5	8.5	2.5
	Weathered		Leached	Weathered		Leached
Control	58.8		51.0	33.0		26.0

\* Its retention : 37, 73, 375 (Kg/cu.m.  $\times 10^{-2}$ )

of 0.05, 0.1 or 0.5%, and injected by the reduced pressure process. *Coriolellus palustris* and *Coriolus versicolor* were selected as wood decaying fungi. Other experiment procedures were the same as above.

The results are shown in Table 5. Again TBT fumarate and TBT terephthalate were superior. The only water-soluble TBT sulphamate showed a pretty good activity. Much attention should be paid to the fact that this compound is adsorbed by the wood constituents and in spite of its water solubility is hardly desorbed by water. When the retentions were small, the phosphor-containing compounds showed the sharp drop of effectiveness. This phenomenon is undesirable for wood preservation. At the smaller retention the difference arising from the kind of the fungus significant. As a whole, *Coriolellus palustris* seems more resistant than *Coriolus versicolor*.

### Summary

The relation between the fungicidal activity and the formula of tributyltin compounds ( $\text{Bu}_3\text{SnX}$ ) is defined. The fungicidal activity is due chiefly to  $\text{Bu}_3\text{Sn}$  residue and a little to X in compound.

It is found that the following organotin compounds remain substantially stable for the light exposure.

TBT-terephthalate, -furoate, -fumarate, -chloride, -p-toluensulfonate and -acetate.

The preservative activity of organotin compounds may be highly estimated. In particular, it is noticeable that TBT-fumarate, -terephthalate, -sulphamate are more active than so far investigated and reported TBT-oxide or -chloride.

### Note

In this report, Clause 4 and 5 are applied to part 9 of Studies on the Organotin Compounds as the Wood Preservatives.

### 摘 要

新しい型の tributyl 系有機錫化合物42種について、寒天希釈法により木材腐朽菌に対する殺菌限界濃度と、光線照射による菌糸生育阻害度の変化と、これらの結果より選出した化合物16種についての Soil-block 法による防腐効力とを検討した。

Tributyl 系有機錫化合物の殺菌力は  $\text{Bu}_3\text{Sn}$  基に存在し、その殺菌力はかなり高い。とくに低濃度における菌糸生育阻害度は、従来の木材防腐剤に見られないほど高いことが注目される。さらに耐光性は大きく、とくに TBT-terephthalate, -toluate, -furoate, -fumarate などは著しい。これに反し、可溶化性で長い側鎖を持った化合物は光に対して不安定である。

Tributyl 系有機錫化合物の防腐効力は dibutyl 系化合物のその10倍程度の効力を有し、

耐候操作によりその差はさらに広がる。PCP-Na と比較した場合、耐候操作を行なわないときは、約2倍の濃度の PCP-Na の効力に相当するが、耐候操作を行なったときは、約20倍の効力に相当する。Tributyl系化合物では、耐光性と密接な関係が存在し、耐光性の大きいものが防腐効力大という傾向がある。とくに注目される化合物は、TBT-fumarate, terephthalate であった。

#### Literature Cited

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